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MODELING PROCESSES IN OXIDE-SILICATE SYSTEMS TREATED BY PLASMA FOR THE PURPOSE OF IMPROVING COATING QUALITY

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Modeling of high-temperature processes in oxide-silicate systems under the effect of plasma is performed. The research is implemented with plasma guns used in analytical chemistry for atom-emission analysis. The selection of these sources is determined by a simpler method for studying the interaction of plasma with a solid material surface. To refine the specified high-temperature mechanisms, thermodynamic modeling has been performed using the Astra software package.

Contemporary engineering pays great attention to the development of new ceramic materials and technologies enabling modifications of surfaces in known construction materials, including deposition of plasma coatings. The latter are needed for protection from heating, corrosion, eroding effect of high-temperature gas flows, for thermal insulation, and for increasing wear and heat resistance of different structures. Plasma coatings are laminar structures consisting of highly deformed particles that have been crystallized at a high rate. The technology for depositing plasma coatings makes it possible to impart new properties to known materials [1]. Plasma technologies determine prospects for new trends in the construction industry [2]. The need for such materials and technologies is constantly growing due to the emergence of new sectors of engineering, which are characterized by rapidly growing work loads, temperatures, and working media aggressiveness.

The present study models high-temperature physicochemical processes occurring in refractory materials and vitreous coatings applied to construction products under the effect of highly concentrated plasma flows. The refractory materials selected for research were bacor and bacor-based coatings produced by plasma-arc melting and spraying for the purpose of restoring corroded blocks of glass-melting furnaces. The studies involved excitation sources used in analytical chemistry for atom-emission analysis (AEA). This choice, on the one hand, is due to the proximity of technological temperatures and, on the other hand, to the possibility of using a simpler method for thermodynamic calculation of high-temperature processes. Such an approach makes it possible to estimate and identify possible directions of reactions in interaction of plasma flow with a solid body surface depending on temperature (plasma energy) and subsequently verify the calculation results using spectral-emission analysis.

The investigated samples in the form of large grains of total weight 0.05 g were placed into a graphite container (the latter also served as one of the graphite electrodes in generating plasma) and treated using low-temperature plasma. The plasma gun power was 8 kW, and the current strength was 20 A. The plasma gun was combined with a ISP-30 spectrograph used to study the evaporation processes. The calculations of working temperatures of arc-discharge plasma were performed using the Ornshtein method consisting in measuring relative intensity of spectral lines with known excitation energy [3]. The latter was carried out selecting the thermometric pair of spectral lines of zinc ($\lambda_1 = 307.2$ nm, $\lambda_2 = 307.6$ nm), which was introduced into the sample in the form of ZnO (0.3 wt.% zinc). The excitation energy of the selected lines is as follows: $E_1 = 8.08$ eV, $E_2 = 4.01$ eV. The calculation was carried out using the formula

$$T = \frac{20{,}510}{2.58 + \log \dfrac{I_{307.6}}{I_{307.2}}},$$

where $I_{307.6}$ and $I_{307.2}$ are the intensities of spectral lines with $\lambda_1 = 307.6$ nm and $\lambda_2 = 307.2$ nm, respectively.

The initial temperature T between the graphite electrodes was 7000 K. In the course of plasma treatment the products of evaporation of materials considered intensely penetrate the high-temperature zone. Emission spectroscopy was used to register the fraction evaporation dependences (Fig. 1), which makes it possible to determine, on a qualitative level, which components are the most liable to evaporation as a consequence of plasma treatment. The optical density of

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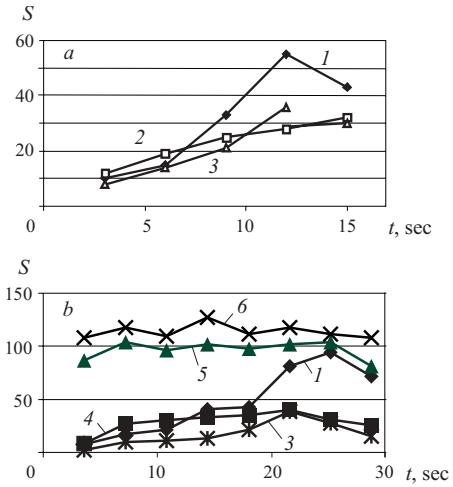

Fig. 1. Dependence of fraction evaporation of components in systems considered under plasma treatment: *a* and *b*) bacor refractories and aluminosilicate glasses, respectively, whose chemical compositions are listed in Tables 1 and 2; *1*, *2*, *3*, *4*, *5*, and *6*) Si, Al, Zr, Ca, B, and Na, respectively.

spectral lines *S* depends on a variation of the element content in plasma during arc-discharge combustion.

The component most intensely evaporating from bacor refractory is silicon dioxide represented in bacor by the vitreous binder. The process of volatilization of silicon dioxide called "sweating" leads to a modification of the chemical composition and improvement of refractory properties, presumably due to a concentration of zirconium dioxide on the surface. Kinetic dependences registered for glass coatings indicate that all oxides making part of glass intensely participate in evaporation processes under plasma treatment; however low-melting components, such as $NaBO_2$ and $NaSiO_3$, do so most intensely.

In order to analyze high-temperature processes occurring in materials under the effect of plasma, thermodynamic computer modeling (TDM) was carried out using the Astra multipurpose software package [4]. The results of TDM of the systems considered, whose compositions are close to those of bacor refractory and glass coating (Tables 1 and 2), are represented in Figs. 2 and 3. It can be seen that in quasiequilibrium conditions, various physicochemical processes can proceed in different temperature ranges, such as evaporation, dissociation, and atomizing of molecules, ionization, excitation, recombination, and emission of atoms.

TABLE 1

Monitored components	Mass content of oxides, %	Variations in composition, %, versus duration of plasma treatment		
		3 sec	9 sec	12 sec
SiO_2	15.0 ± 1.0	14.0 ± 1.0	11.0 ± 1.0	7.0 ± 0.5
Al_2O_3	51.0 ± 3.0	52.0 ± 3.0	53.0 ± 3.0	53.0 ± 3.0
ZrO_2	28.0 ± 1.0	28.0 ± 2.0	30.0 ± 2.0	34.0 ± 2.0

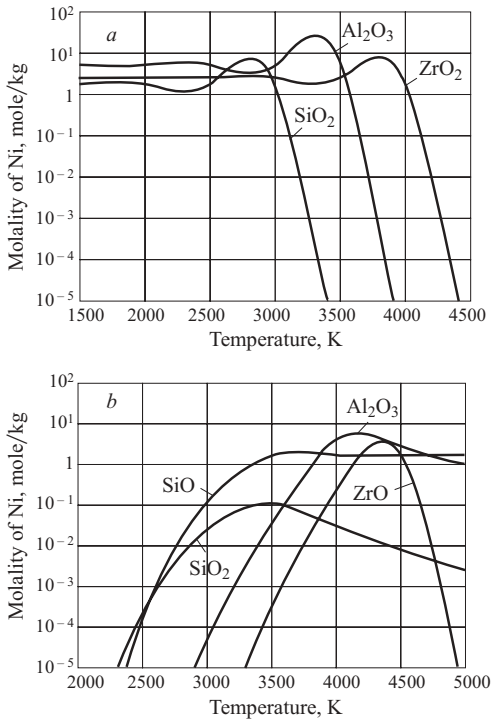

Fig. 2. Fragments of thermodynamic modeling of physicochemical processes in system with a composition corresponding to bacor refractories: *a* and *b*) are the condensed and vaporized state, respectively.

In the case of high-temperature treatment of bacor, condensed phases SiO_2, Al_2O_3, and ZrO_2 disappear at temperatures of 3500, 4000, and 4500 K, respectively (Fig. 2*a*). At first a silicate melt emerges, presumably at temperatures of 2000 – 3500 K, and Al_2O_3 and ZrO_2 gradually pass into this melt enriching it. Along with formation of the melt, intense evaporation processes take place, primarily that of the silicate binder (SiO_2, SiO). At temperatures above 4500 K condensed phases completely disappear, and the composite material passes into a gaseous phase. As temperature further increases, dissociation of oxides and ionization of atoms play a perceptible role.

In the case of high-temperature treatment of glass, silicate melt starts emerging at temperatures close to 1000 K (Fig. 3) and at the same time, intense evaporation of oxygen compounds of alkaline metals in various forms is observed.

TABLE 2

Monitored components	Mass content of oxides, %	Variations in composition, %, versus duration of plasma treatment	
		5 sec	15 sec
SiO_2	63.0 ± 3.0	67.0 ± 3.0	69.0 ± 3.0
Na_2O	15.0 ± 1.0	10.4 ± 1.0	8.0 ± 1.0
BaO	6.3 ± 1.0	6.6 ± 1.0	7.0 ± 1.0
CaO	3.4 ± 0.5	4.0 ± 0.5	4.0 ± 0.5
MgO	3.3 ± 0.5	3.0 ± 0.5	3.0 ± 0.5

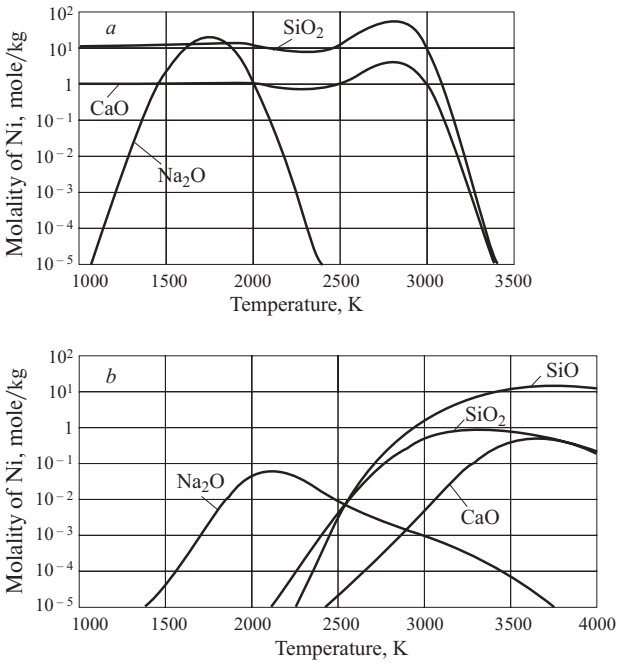

Fig. 3. Fragments of thermodynamic modeling of physicochemical processes in system with a composition corresponding to glass: *a* and *b*) are the condensed and vaporized state, respectively.

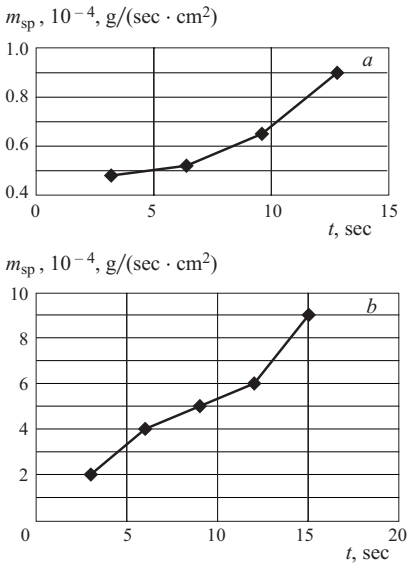

Fig. 4. Dependence of specific evaporation rate m_{sp} on duration t of plasma treatment of bacor refractories (*a*) and aluminosilicate glasses (*b*).

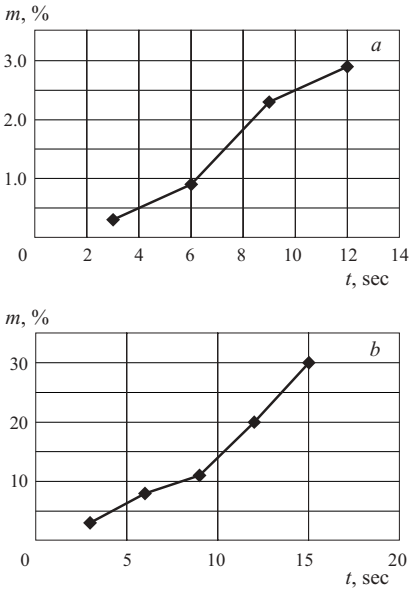

Fig. 5. Variation in material mass m depending on plasma treatment duration t of bacor refractories (*a*) and aluminosilicate glasses (*b*).

At temperatures above 2500 K higher-melting silicon and calcium oxides are involved in the process. At 2500 K electron gas and alkali metal cations start emerging, and above 3500 K all glass components pass into a vaporized state.

Using the gravimetric method, it was established that the effect of plasma on materials considered results in a substantial weight loss. Figure 4 shows dependences of specific evaporation rates on duration of plasma treatment of materials considered. It can be seen that the specific evaporation rate depends both on the nature of material and on treatment duration. As could be expected, glass coatings have lower thermal resistance due to the presence of low-melting components. Bacor mostly contains high-melting oxides; therefore, it has higher thermal resistance than glass. The weight variation after 10 sec of plasma treatment in bacor amounted to 3% and in glass to 30% (Fig. 5).

In order to identify the chemical composition of materials considered before and after plasma treatment, special methods of AEA were developed. The main requirement in this case was bringing the chemical and structural-phase compositions of the reference sample and the sample analyzed in strict correlation. State reference samples Nos. 4166–87 — 4171–87 (a set of standard samples of graphite SOG-28) are the most suitable for analysis of bacor refractories, since they contain all elements needed. Therefore, the main purpose of sample preparation was conversion of bacor to the graphite basis and a correct choice of stabilizing active or neutral carriers.

To bring the sample in strict correlation with the reference standards selected, a bacor sample was consecutively diluted to one-hundredth, providing for the analytical signal getting into the center of the calibration plot constructed on the basis of the specified reference samples. To select a composition for the graphite powder – carrier buffer mixture and optimum AEA conditions, a specialized software package named Spectr was developed, which uses experimental data on intensities of homological pairs to calculate plasma temperature, electron concentration, ionization potential, and duration of atoms' stay in the discharge zone. It follows from the calculation results that in determining the basic composi-

tion of bacor, one should introduce 5 wt.% CuO as a carrier into the buffer mixture composition. Its use shortens the stay of atoms in the discharge zone while maintaining intense ionization of bacor sample atoms. This choice of the carrier is also validated experimentally, since it gives better reproducibility of results.

The reference samples for AEA of glass coatings were prepared in accordance with requirements of OST SL-97/1 used for estimation of quality of electrotechnical glasses. As glasses are multicomponent systems, to remove the mutual effect of the components during the formation of analytical signals, a special buffer mixture of composition $SrCO_3$ – CuO – C was selected, which after diluting the sample in a ratio of 1 : 10 yields reliable results. The reliability of results was verified based on *t*-criterion comparing to the certified value of the reference glass. The relatively low error in AEA is due to registering the analytical signal using a multichannel emission-spectra analyzer with a special program for statistic processing of measurement results. The AEA data are listed in Tables 1 and 2.

Plasma treatment of bacor refractory decreases the mass content of SiO_2 from 15 to 7%, whereas the content of ZrO_2 increases from 28 to 34%, which is a favorable factor (ZrO_2 determines the corrosion resistance of bacor to glass melt). Plasma restoration of refractories is expected to improve their corrosion properties. Plasma treatment has a significant effect as well on the composition of glass coatings. A decrease in the quantity of alkali metal compounds and other low-melting components and, accordingly, an increase in the content of the main glass-former SiO_2 in glass primarily modifies the thermophysical properties of the material. Consequently, a change, for instance, in the TCLE of the coating differently from the TCLE of the substrate may cause its peeling under cooling.

The studies performed established that oxides under the effect of plasma consecutively evaporate from the bacor refractory in accordance with their melting temperatures and, consequently, the surface layer composition is modified and becomes more fire-resistant. In the formation of protective-decorative glass coatings to protect the initial composition, one should decrease the duration of plasma treatment The experiments indicate the need for taking into account the mutual effect of oxides in atom-emission analysis of these materials.

The recommendations described above have practical significance for improving the quality of coatings produced using plasma technology. The methods of atom-emission analysis can be used for analytical control of the properties of building materials at construction production facilities.

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